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Surface processing of TlBr for improved gamma spectroscopy

Lars F. Voss, Adam M. Conway, Robert T. Graff, Patrick R. Beck, Rebecca J. Nikolic, Art J. Nelson, Stephen A. Payne, Hadong Kim, Len Cirignano, and Kanai Shah

Abstract–**Planar detectors have been fabricated on 0.5 mm thick TlBr crystals grown by Radiation Monitoring Devices (RMD). The crystals have been characterized by microhardness measurements. A surface damage layer resulting from mechanical polishing has been measured to be approximately 3.7 μm thick. We have removed this layer with H_2O_2 chemical etching and compared device performance with and without the presence of the surface damage layer and found significant differences in the initial and long term current-voltage behavior and radiation response. Detectors treated with H_2O_2 to remove this layer have been shown to display superior performance as compared to unetched detectors followed a period of "field annealing".**

I. Introduction

Thallium bromide shows significant promise as a room temperature gamma detector, with resolution of <1.2% having been demonstrated [1]-[4]. However, detectors are presently limited by polarization phenomena. This is attributed to the fact that TlBr is a mixed electronic-ionic conductor, with the ionic current being significant at room temperature. The role of the crystal surface in TlBr detectors is believed to be critical issue [5]. At room temperature, a large concentration of Schottky pairs (VTl- + VBr+) exists due to their low formation energy of 1.1 eV [6]. In addition, VBr+ has a low barrier to migration (0.25 eV), rendering it highly mobile within the lattice [6]. Under applied bias, an imbalance in the distribution of these charged vacancies results in the build-up of an internal electric field that opposes the applied bias and thereby decreases carrier collection efficiency.

Several approaches to reducing this polarization have already been reported. The first is to cool the detectors down to -15°C or lower, which serves to decrease both the vacancy concentration and their mobility [7]. Detectors operated at sufficiently lower temperature show no signs of degradation, even under long-term applied bias. The second approach is to apply Tl metal contacts to the crystals; the bias is then reversed roughly every 24 hours in order to maintain stable

operation, which appears to be indefinite under these conditions at room temperature [8]. While both of these approaches act to increase the operational lifetime of TlBr detectors, the first can be power intensive for portable devices due to the cooling requirement and the second requires the use of Tl metal, which is highly toxic and can be readily absorbed through the skin and moreover benefits from switching of the voltage polarity which may not be compatible with single carrier charge sensing techniques. Thus, an alternative method to control the polarization of these detectors is desired. In this work, we show that the presence of near surface damage created by mechanical polishing has a significant effect on long term polarization behavior of TlBr planar detectors and that its removal can be beneficial for their stability.

II. Fabrication and Results

Because of the low hardness of TlBr, mechanical polishing creates a large amount of damage, likely manifesting itself as dislocations oriented parallel to the surface being polished as well as other types of induced disorder to the crystallinity. It is expected that this damage plays a large role in the behavior of TlBr detectors. The extent of this damage layer can be measured using microhardness techniques [9]. By monitoring the Vicker's hardness versus indentation depth, an exponential fit can be deduced. The intersection of this line and the bulk hardness, reported to be approximately 70 MPa [9], indicates the thickness of the polishing damage layer. Fig. 1 shows the plot of Vicker's hardness vs indentation thickness, which indicates a damage layer of approximately 3.68 μm.

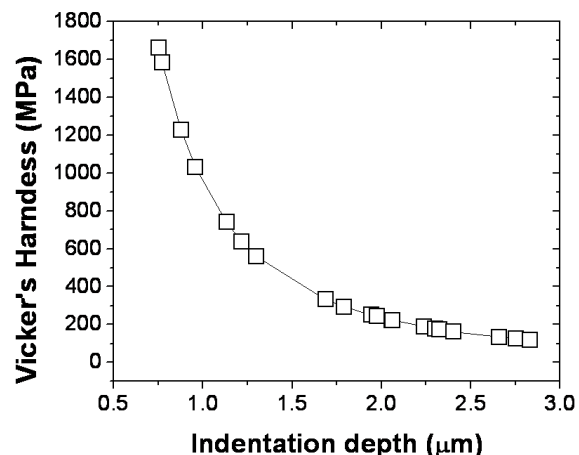Fig. 1. Vicker's hardness vs indentation depth for polished TlBr crystal.

In order to gently remove this damage layer, chemical etching has been employed. For this, we have used 15% H_2O_2 in H_2O. The observed etch rate is approximately 100 nm/minute. H_2O_2 acts to etch TlBr through a sequential oxidation/removal process, as the resultant Tl2O is soluble in water. The reaction is expected to be $2TlBr(cr) + H_2O_2 \rightarrow Tl_2O(aq) + H_2O + Br_2$. This process leaves the atomic composition of the TlBr surface unchanged relative to the polished (pre-processed) state, which was confirmed by X-ray Photoelectron Spectroscopy (XPS) measurements, shown in Table I. The ratio of Tl:Br and their bonding states are unchanged for the pre-etched and etched samples. This makes H_2O_2 ideal for studying to effect of surface damage removal on detector performance. Note that the concentration of O is decreased; this is attributed to the smoother surface after etching, resulting in less surface area to oxidize. In addition to damage removal, surface roughness is also decreased with chemical etching.

TABLE I. XPS CONCENTRATIONS FOR TL, BR, AND O OF UNETCHED AND ETCHED CRYSTALS.

TlBr Samples	Tl	Br	O	Tl :Br
As polished	35.5	25.9	38.6	1.4
15% H_2O_2	44.8	32.5	22.7	1.4

Atomic Force Microscopy (AFM) measurements have been performed to monitor this, with varying concentrations of H_2O_2. Fig. 2 shows the surface roughness for these concentrations after one hour of etching. The root mean square (RMS) roughness decreases to similar values in the range 15-20 nm regardless of the concentration. Fig. 3 shows the morphology of the surface for unetched and 15% H_2O_2 etched samples; note that the presence of hillocks on the surface remains even as the RMS roughness decreases.
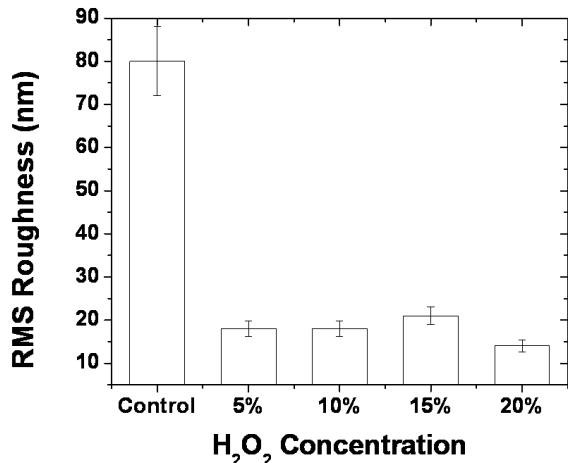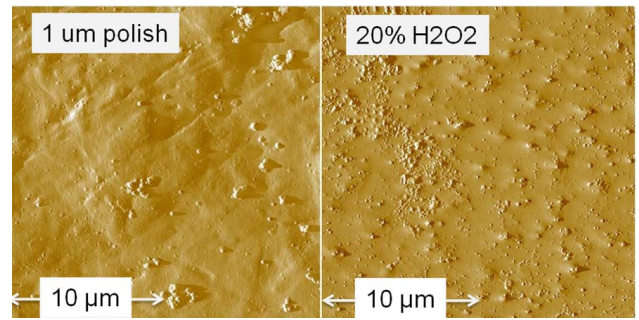

Fig. 2. RMS roughness vs H_2O_2 concentration.

Fig. 3. AFM surface scans of (a) polished and (b) polished and etched TlBr.

The detector to be etched was subjected to 15% H_2O_2 treatment for a total of three hours before electrode deposition, with the goal of removing 15-20 μm of material. This was to ensure that the entire damage layer was removed. Au electrodes were then deposited using a shadow mask on both the etched and unetched sample using a thermal evaporator with a base pressure of 4×10^{-6} torr. The deposition rate was maintained at 1.3-1.5 Å/s during the deposition, with a target thickness of 1500 Å. The temperature of the TlBr was monitored with a thermocouple, and reached a maximum of 60oC during the deposition.

Fig. 4 shows the long term behavior of both the etched and unetched detectors. Initial measurements of an [241]Am induced 60 keV spectrum were performed, followed by current vs time (I-t) measurements over a period of 45 hours without irradiation at 100V. After this, the [241]Am spectra were remeasured. For the unetched detector, a peak is initially present. Monitoring the I-t response, a significant decrease is initially observed, consistent with observed polarization behavior reported in the literature. Upon reintroduction of the [241]Am source, the peak position is shifted to lower energy, indicating decreased charge collection as a result of the buildup of an internal field.

The detector etched with H_2O_2 displays significantly different behavior. Initially, the noise floor of the detector is large despite the comparable initial current and no peak is present when irradiated with 241Am. The I-t measurement shows an initial decrease in the current, similar to that observed with the unetched detector. However, this trend is reversed after 1 hour and an increase in current is observed which reaches a maximum increase of 2x after 18 hours and begins to decrease again. Eventually the current decreases to the initial current value after a period of 45 hours. When the [241]Am source is reintroduced, a peak is now present. Under continued operation, this peak remains at the same energy and shows the same amplitude and full width half maximum (FWHM). Performance was observed to be stable for the duration of the measurement, which was 72 hours.

We attribute the difference in the performance of these detectors to the removal of the heavily damaged polish layer. In the case of the unetched sample, the polished surface could act to impede the motion of vacancies and could also act as vacancy sinks, essentially trapping them. This imbalance in

the mobility would result in a buildup of vacancies and thus reduce the internal electric field. For the etched sample, this buildup initially occurs due to an imbalance in the electrochemical reaction rate at the surface and the motion of the charged vacancies within the bulk. After some time, this results in an accumulation of charge directly under the electrode. This accumulation of charge leads to a lowering of the electronic barrier height of the contact, resulting in increased electronic injection and thus the observed increase in the current. Over time, a balance is reached between the arrival and removal of charged vacancies at the electrode and the current returns to its initial value, which we are calling "field annealing".
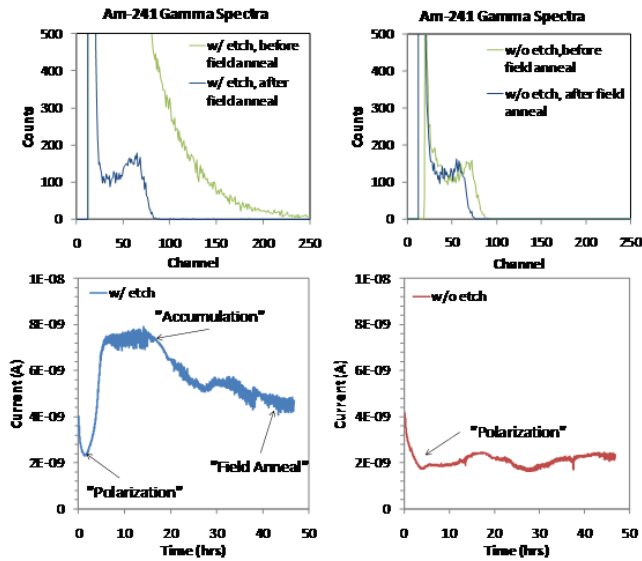

Fig. 4. Current vs time and ^{241}Am spectra for etched and unetched Au/TlBr/Au planar detectors.

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